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Determination of the Insect Growth Regulator Methoprene in Natural Waters by Capillary Gas-Liquid Chromatography

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DETERMINATION OF THE INSECT GROWTH REGULATOR METHOPRENE IN NATURAL WATERS BY CAPILLARY GAS-LIQUID CHROMATOGRAPHY

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ABSTRACT

Residues of methoprene were measured in natural waters by capillary gas-liquid chromatography (GLC). Methoprene was extracted in the field by liquid-liquid partitioning with dichloromethane, transported to the laboratory, and extracted a second time with hexane. The extracts were dried with Na_2SO_4 and analyzed by Capillary GLC on a 15m x 0.25mm, DB-5 capillary column using a hydrogen flame ionization detector. The recovery of methoprene from natural waters was 107.6 ± 20.2% (n=18). Methoprene was detected in 3 of 5 sites sampled and ranged from 0.39 to 8.8 ug/L.

INTRODUCTION

Methoprene (isopropyl (2E, 4E)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate), is an insect growth regulator developed in early 1970 for control of diptera larvae (1-7). The use of methoprene by mosquito control organizations has increased with the development and introduction of a controlled release briquet formulation (Altosid^R, Zoecon Corp.). To date, no literature on the environmental concentrations of methoprene resulting from the controlled release formulations was found.

The U.S. Environmental Protection Agency, Environmental Research Laboratory at Duluth is charged with developing methods to assess the environmental impact of a wide variety of chemicals. Methoprene is a member of an increasingly popular class of pesticides for which little environmental chemistry data exists. An ecological risk assessment cannot be made without knowing or accurately estimating the potential exposure concentration for organisms living in the treated water.

Current analytical methods for methoprene utilize packed column GLC (8-10). Although these methods are sensitive to sub-ug/L concentrations, packed columns have low efficiency and thus poor resolution of co-extractives which can result in questionable analyte identity, interferences, and decreased sensitivity. More recently, capillary GLC using high efficiency columns has allowed for improved separation of sample co-extractives frequently encountered in environmental samples resulting in more reliable analyte identification and quantification.

The objectives of this study were two-fold; first, to develop a capillary GLC method for the analysis of methoprene in natural waters at sub-ug/L levels, and second, to collect and analyze field water samples from a variety of aquatic habitats where Altosid^R

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from natural waters fortified with 1.25 ug/L in the laboratory and at the field site was 97.1 ± 11.8% (n = 9) and 118.2 ± 21.9% (n = 9), respectively. The overall recovery from laboratory and field fortified samples was 107.6 ± 20.2% (n = 18).

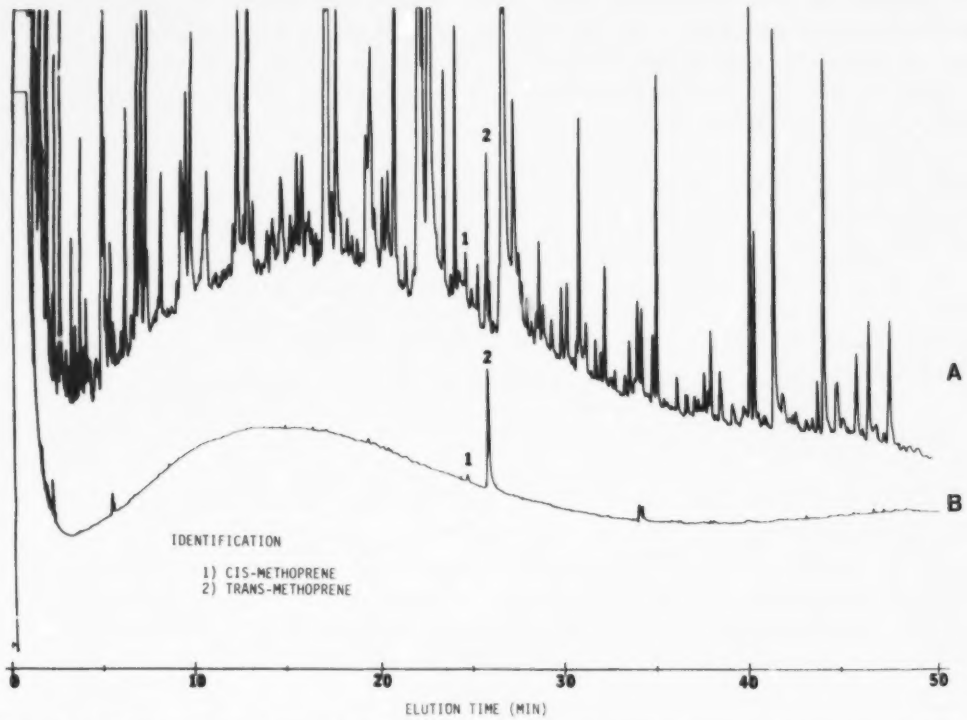

Figure 1. Capillary gas chromatograms of a natural water sample extract (concentrated 1000 times) which contained 1.40 mg/L methoprene (A), and a reference standard containing 1.25 mg/L methoprene (B). Chromatographic conditions are stated in the text.

The mean gas chromatographic retention time relative to the time of injection for trans-methoprene over the entire study period was 25.68 ± 0.026 min. (n = 45), and the percent coefficient of variation (%CV) was 0.10%. The highest within run analytical variability observed had a mean retention time of 25.66 ± 0.026 min. (n = 7, %CV = 0.10). The lowest within run variability observed was 25.69 ± 0.013 min. (n = 7, %CV = 0.051). In all of the individual analytical runs, the retention time precision was equal to or better than the overall system precision. The stability of the analysis system as demonstrated by the retention time statistics allowed confident identification of methoprene.

An emulsion problem was encountered during the initial dichloromethane field extraction step. Most samples created little difficulty, however, in serious cases, the non-emulsified portion of solvent was removed and dried. The hexane added during the second extraction step combined with the remaining emulsified dichloromethane produced a sufficiently clear extract with no measurable effect on methoprene recovery. If an emulsion still persists after this step, alternate procedures such as centrifugation, freezing or the addition of salt may need to be investigated. Field samples must be preserved immediately upon collection in the field due to rapid decomposition of methoprene by microorganisms and sunlight (11-13). Extraction of the water samples at the field site was essential for preserving the samples and proved to be a simple, convenient technique which prevented degradation and allowed samples to be transported and stored for at least two days prior to subsequent processing. Other researchers have utilized acetonitrile (12) and acetone (9) to extract and preserve water samples.

Sites which are treated with Altosid^{R} briquets vary considerably in the amount of dissolved and particulate organic matter. Chromatograms that indicate large amounts of co-extractable organic compounds which interfere with identification and quantification of methoprene should be subjected to further clean-up procedures using florisil or other suitable adsorbants (8-10).

Environmental Levels of Methoprene

Water samples were collected from five different aquatic habitats to validate the method and determine the environmental levels resulting from the use of Altosid^{R} briquets. Five aquatic sites representing different habitat types were sampled on three separate dates. Methoprene was detected in three of the five sites sampled ranging in concentration from 0.39 to 8.8 ug/L (Table 2). Two sites, a roadside ditch and a woodland

Table 2. The concentration (ug/L) of trans-methoprene measured in field water samples from sites treated with Altosid^{R} briquets, 1986.

	trans-methoprene concentration, ug/L		
Habitat type	May 28	June 27	August 7
Grassy Meadow	<0.20[1]	0.39	<0.20
Roadside Ditch	<0.20	<0.20	NS[2]
Woodland Pond	<0.20	Dry	Dry
Cattail Pond	<0.20	0.97	Dry
Grassy Cornfield Wetland	NS	1.4/8.8[3]	2.31

[1] detection limit = 0.2 ug/L

[2] Site not sampled on date indicated

[3] Duplicate field sample

pond, never contained any detectable residues (> 0.2 ug/L). The woodland pond was dry after the first sampling date and the roadside ditch maintained a constant water volume throughout the summer. The highest methoprene concentration of 8.8 ug/L was found in a grassy wetland surrounded by a tilled cornfield. The site contained water only after rainfalls of several inches and the water sample was collected in a plow furrow located in the center of the site.

Aquatic sites treated with Altosid^{R} briquets for mosquito control vary in the amount of water and aquatic vegetation. Due to the nature of the habitat and the uneven distribution of briquets at each site, methoprene is not equally distributed in the site water and grab samples from a single location may seriously misrepresent the actual concentration. The duplicate sample taken on June 27 at the grassy cornfield wetland site measured 1.4 ug/L and 8.8 ug/L. This may be due to the unequal distribution of methoprene at this site; however, no conclusions can be drawn from a single sample. A composite sample as described in this study, or a large number of replicate samples that encompass both horizontal and vertical distribution patterns may be the best way to properly quantify the amount of methoprene. For field studies of this nature, standardized quality assurance procedures are essential for the positive identification and quantification due to the large number of co-extractives, high sampling variability, and natural site diversity. If available, GC/MS analysis is recommended for confirmatory work (9, 14).

The sample collection, extraction and analysis procedures described worked well and had good recovery for the analysis of methoprene in a variety of environmental waters. The procedures are simple and the capillary system described exhibited good resolution and sensitivity.

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